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## ORIGINAL ARTICLE

### 1st Nano Update

# Characterization of Mn doped ZnS nanocrystalline powder dispersed in polyvinyl alcohol

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**Abstract** Manganese doped zinc sulfide nanocrystalline powder was synthesized with sodium citrate and its films were formed by mixing it with polyvinyl alcohol to study optical absorption of Mn doped ZnS dispersed in polyvinyl alcohol. The characteristics of the prepared powder and film samples were studied by X-ray diffraction, transmission electron microscopy and UV–visible absorption spectroscopy. Samples exhibited optical absorption at lower wavelength region and particle sizes were calculated from X-ray diffractogram.

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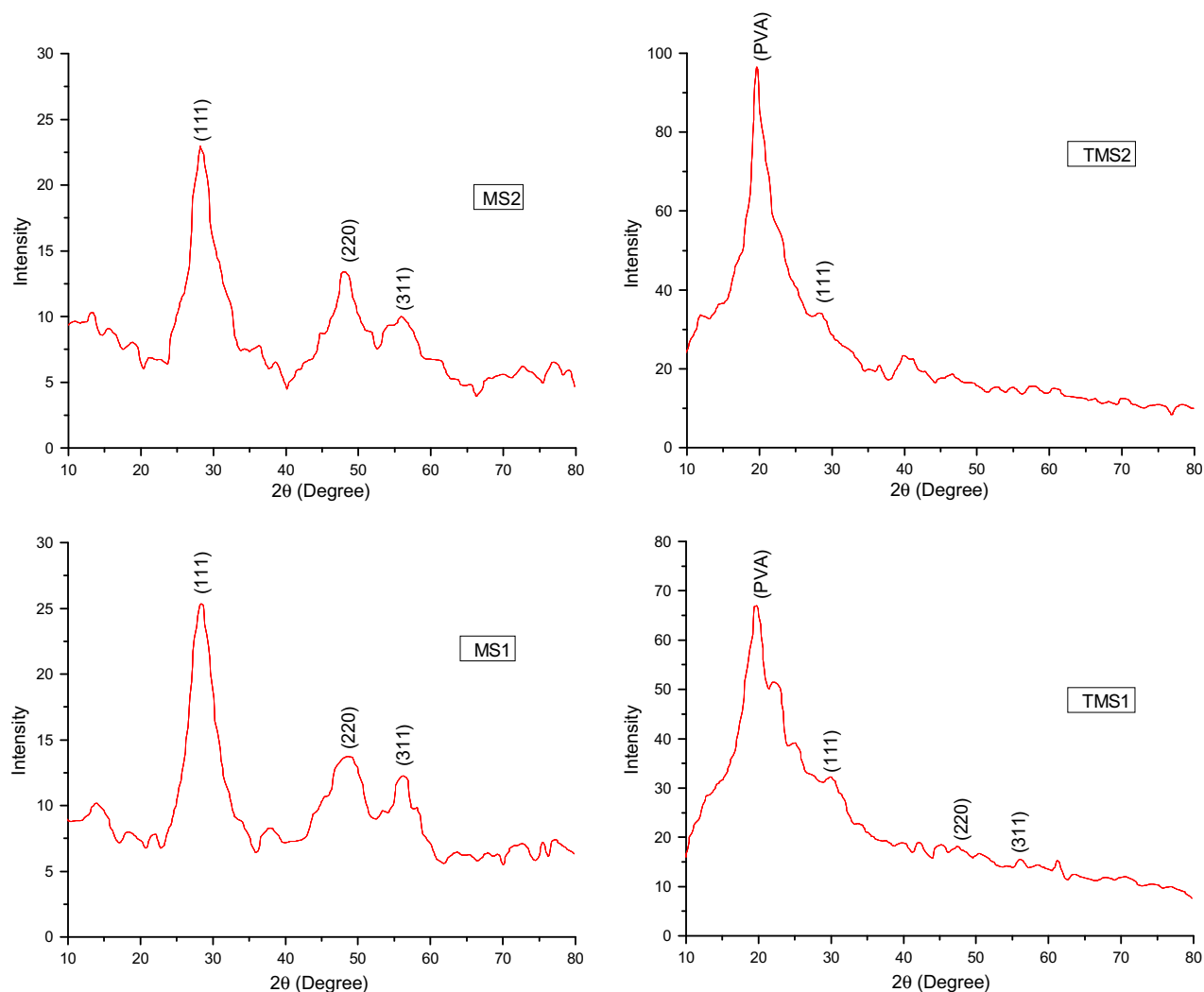
## 1. Introduction

Nanomaterials caught the attention of researchers due to its peculiar properties arising from its increased surface to volume ratio and changed electronic structure due to quantum confine-

ment effect (Abdul Kareem and Anu Kaliani, 2010; Abou El-Nour et al., 2010; Kozák et al., 2010; Yuan and Zhu, 2010; Dong et al., 2010; Steitz et al., 2008). The number of surface atoms increases as the materials becomes smaller and its surface energy increases. This increased surface energy and quantum confinement effect have a tremendous effect on the absorption spectra and photo luminescence. ZnS:Mn has attracted much interest due to its luminescence characteristics since Bhargava et al. (1994), because they have reported that the photoluminescence of  $Mn^{2+}$  ions in ZnS nanocrystals had a very high quantum efficiency with a luminescence decay several orders of magnitude faster than in the bulk crystals. The optical properties of manganese doped zinc sulfide nanocrystalline powder, synthesized in the presence of sodium citrate by chemical precipitation method and with polyvinyl alcohol for making films are reported here. The special interest on ZnS:Mn is due to its high photoluminescence efficiency and

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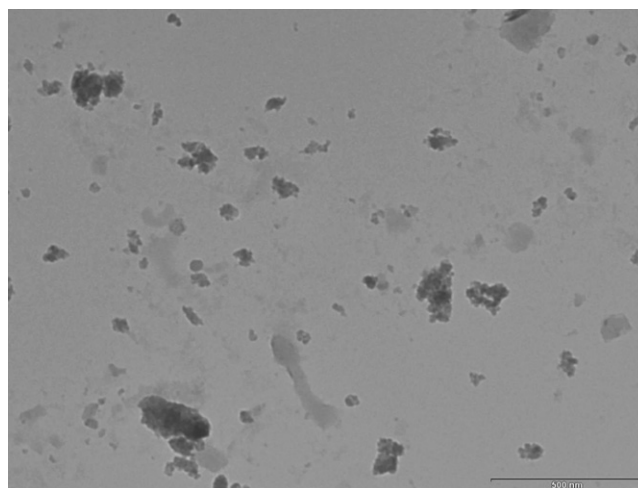


**Figure 1** X-ray diffractogram of the samples.

stability at ambient temperature, these are critical properties required for luminescence devices and it also considered as an ideal candidate material for a fluorescence bio-labeling due to its long luminescence life time (Balaz et al., 2002; Yang et al., 2003; Grmela et al., 2008; Hamaguchi et al., 2008; Hwang et al., 2006).

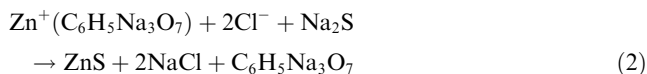
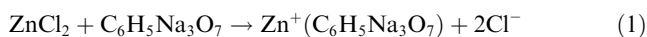
## 2. Experimental

The nanocrystalline powder synthesis was carried out in an environment friendly manner in de-ionized water at room temperature and under ambient conditions. One molar aqueous solution of  $ZnCl_2$  and  $MnCl_2$  (0.1 M for MS1 and 0.05 M for MS2) was mixed under continuous magnetic stirring in the presence of sodium citrate solution of 0.5 M. White precipitate was formed when aqueous solution of 0.5 M  $Na_2S$  was added drop wise into the master solution. The white precipitate was filtered and washed thoroughly four times in de-ionized water, finally washed in ethanol and dried under  $50^\circ C$  in air to make it fine powder. But, the color of the powder samples changed to light yellow from white after all the water contents



**Figure 2** TEM image of the sample MS1.

dried out. The light yellow color of the powder sample may be due to the excess of the sulfur atoms:



For studying its film formation with polyvinyl alcohol, the solution of polyvinyl alcohol (0.03 g/ml) was heated to 60 °C and continuously stirred for half an hour to make it a homogeneous solution. The prepared nanocrystalline powder had been dispersed in deionized water, and slowly added into hot polyvinyl alcohol solution. Heating and stirring continued until the solution became thick and then cleaned glass slides were dipped into this to make films and the films named as TMS1 (film made out of powder MS1 sample) and TMS2 (film made out of powder MS2 sample).

The samples were characterized by UV-Visible Spectroscopy (Varian, Cary 5000), X-ray Powder Diffractometer of Bruker AXS D8 Advance and scanned the samples from 3° to 80° with steps 0.010° and 0.2 s at 25 °C. The transmission electron microscope image was obtained from transmission electron microscope of Philips, Holland Model – Tecnai 20.

### 3. Results and discussion

The observed XRD peaks in Fig. 1 matches well with the cubic crystal structure of standard ASTM card No. 77-2100 for the ZnS crystals. The addition of  $\text{Mn}^{2+}$  into the ZnS crystal structure replaced some  $\text{Zn}^{2+}$  ions and it has also reduced the size of the crystals due to the smaller atomic radius of the  $\text{Mn}^{2+}$  when compared to the  $\text{Zn}^{2+}$ . The ions  $\text{Mn}^{2+}$ , by replacing  $\text{Zn}^{2+}$ , practically do not introduce any noticeable distortions to the XRD spectrogram of the ZnS crystals (Bulanyi et al., 2005; Lawther et al., 1978; Murphy et al., 2007). Further the TEM image given in Fig. 2 shows that the particles sizes are below 500 nm and it also shows that the nanocrystals are agglomerated to make larger particles.

Crystallite sizes were calculated from the X-ray diffractogram using Scherrer's formula and the average crystallite sizes were found as 3.05, 3.29, 16.0 and 26.3 nm for MS1, MS2, TMS1 and TMS2 samples, respectively. The observed  $2\theta$  values and the inter planar spacing ' $d$ ' are shown in Table 1 for each sample. From Fig. 1, it is observed that the diffraction peak of the nanocrystals become unambiguous and is reduced much in the ZnS:Mn-PVA film samples because of the coating of polyvinyl alcohol over the ZnS:Mn nanocrystalline powder. From Table 1 it is seen that the crystallites were agglomerated and formed larger crystallites in the film samples and this may be due to the non-uniformity of the dispersion.

The study of optical absorption is important to understand the behavior of semiconductor nanocrystals. A fundamental property of semiconductors is band gap; the energy separation between the filled valence band and the empty conduction band. Optical excitation of electrons across the band gap is strongly allowed, producing an abrupt increase in absorption at the wavelength corresponding to the band gap energy. Absorption maxima of the prepared materials are found from the optical absorption spectra and are shown in Fig. 3. The absorption peak is blue shifted when compared to the absorp-

**Table 1** Crystal information from the X-ray diffractogram of the samples.

ASTM 77-2100	Observed values											
	$h\ k\ l$			MS1			MS2			TMS1		
	$2\theta$ (deg.)	$d$ (Å)		$2\theta$ (deg.)	Crystallite size (nm)	$d$ (Å)	$2\theta$ (deg.)	Crystallite size (nm)	$d$ (Å)	$2\theta$ (deg.)	Crystallite size (nm)	$d$ (Å)
28.53	3.1263	(1 1 1)		28.58	3.26	3.1198	28.24	2.83	3.1568	29.67	26.2	3.0076
47.454	1.9144	(2 2 0)		47.13	–	1.9267	48.41	3.77	1.8788	47.39	10.2	1.9165
56.307	1.6326	(3 1 1)		56.33	2.85	1.6318	56.21	–	1.63517	56.36	11.7	1.6310
Average crystallite size (nm)				3.05		3.29			16.0		26.3	

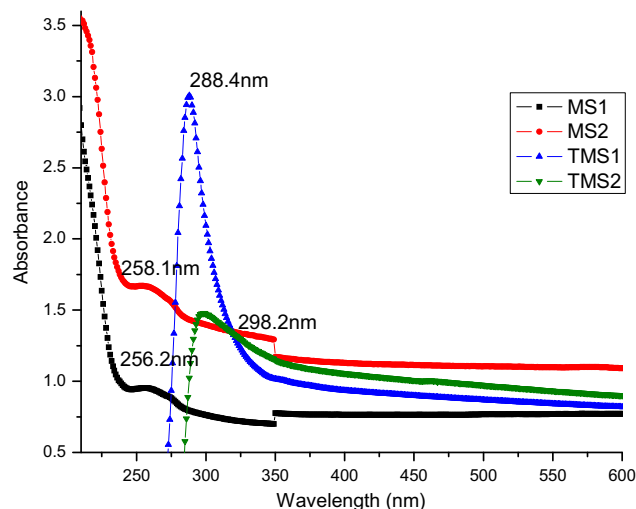


Figure 3 Absorption spectra of the samples.

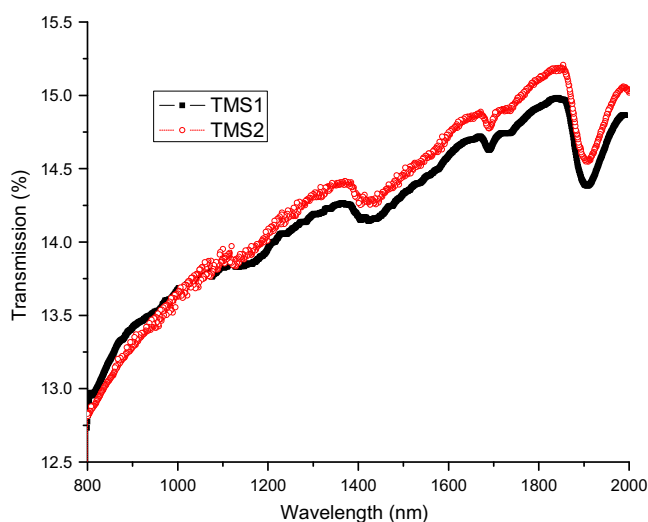


Figure 4 Transmission spectra of the film samples.

tion peak (332 nm) of the bulk material. This shift is due to the quantization effect that the band gap increases with the size reduction of crystallites, which is observed in the X-ray diffractogram also. The band gap of the samples were calculated as 4.84, 4.80, 4.29 and 4.16 eV for samples MS1, MS2, TMS1 and TMS2, respectively. The absorption of film samples has been red shifted when compared to the powder samples because of the formation of larger crystallites as seen from the X-ray diffractogram and which is shown in Table 1.

The thickness of the film samples were calculated from the envelop method (Swanepoel, 1983) using the transmission spectra. The optical transmission spectrum can be divided into four regions as (1) the transparent region (where the optical absorption coefficient,  $\alpha = 0$ ) where the transmission is determined by refractive index ' $n$ ' of the film and the refractive index of the substrate ' $s$ ' through multiple reflections, (2) weak absorption region, where  $\alpha$  is small and the transmission starts to decrease, (3) medium absorption region, where  $\alpha$  is large and the transmission decreases mainly due to the effect of  $\alpha$  and (4) strong absorption region, where the transmission decreases considerably only due to the influence of  $\alpha$ .

The film thickness can be obtained from the refractive index corresponding to the adjacent extreme values as given below

$$d = M \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)} \quad (3)$$

It is assumed that the proportionality constant  $M = 1$  for two adjacent maxima or minima. Refractive index ' $n$ ' of the film can be obtained from the equation:

$$n = [N + (N_2 - s_2)1/2]1/2 \quad (4)$$

where

$$N = 2s \frac{T_M - T_m}{T_M T_m} + \frac{s_2 + 1}{2} \quad (5)$$

' $s$ ' is the refractive index of the substrate (here for glass,  $s = 1.53$ ),  $T_M$  is the transmission maximum and  $T_m$  is the transmission minimum. Adjacent transmission maxima ( $T_M$ ) and minima ( $T_m$ ) for all the corresponding wavelengths ( $\lambda_1$  and  $\lambda_2$ ) from 500 to 2000 nm were found from Fig. 4 to calculate the thickness of the films and the average thickness is calculated as 19.44  $\mu\text{m}$  for TMS1 sample and 21.21  $\mu\text{m}$  for TMS2 sample.

#### 4. Conclusion

Manganese doped zinc sulfide nanocrystalline powder had been synthesized with sodium citrate and its films were formed by mixing with polyvinyl alcohol. X-ray diffractogram of the powder samples showed smaller crystallites, while the X-ray diffractogram of film showed larger crystallites when the smaller crystallite powder was mixed with polyvinyl alcohol.

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